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Recent NMR investigations on molecular dynamics of polymer melts in bulk and in confinement

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ABSTRACT

Polymer dynamics in the melt state cover a wide range in time and frequency, for both molecular weights below and above the entanglement length. Nuclear Magnetic Resonance (NMR) offers a number of techniques that cover a broad section of this frequency range, with frequency dependent (i.e., magnetic field dependent) relaxometry providing the widest window. Combining fast field cycling techniques with frequency–temperature superposition has recently improved the understanding of polymer melt dynamics from the local to global range. At the same time, a detailed theoretical approach that separates intra- and intermolecular contributions to relaxation times has been developed. These methods are shown to improve the description of segmental dynamics in polymers, being related to time-dependent diffusion coefficients, and to distinguish between these two different relaxation contributions for a number of model compounds. The findings represent the foundation for a more thorough understanding of polymers under external restrictions and bear potential to provide a conceptually new access to biopolymer dynamics and interactions.

1. Introduction

In this review, we summarize new experimental results using NMR relaxometry and theoretical descriptions of the spin–spin dipolar coupling effects of polymer melts that have recently been presented in the literature and have shown to converge towards a more detailed description of polymer chain dynamics in the melt state. A particular aspect in these studies covers the relative importance of intra- and intermolecular dipolar interaction to relaxation for the most ubiquitous NMR active nucleus, the hydrogen atom. The relative contributions from local and global dynamics can be accessed by frequency–temperature superposition of experimental data that are compiled in a large temperature range. Typically a Larmor frequency range between 10^4 and 10^8 Hz is covered using Fast Field Cycling (FC) relaxometry, where the relative influence of a slow dynamics contributions around and above the entanglement length of the polymer is shown to depend on chain length for linear macromolecules. The different frequency dependence of intra- and intermolecular contributions to the relaxation rate have both been predicted theoretically for the two fundamentally different concepts of isotropic and anisotropic dynamics, and were experimentally proven by recent experiments employing isotopic dilution in perdeuterated polymers of varying concentration.

Following a summary of the most important concepts of polymer melt dynamics in the light of NMR investigations (Section 2), the theoretical background is presented in Section 3. Experimental results for the dipolar correlation function and, derived from it, measures of the mean square displacement and the diffusion coefficient are discussed in Section 4. We conclude with a collection of recent developments and potential applications in bordering fields in Section 5 that discuss the behavior of polymer melts under external restrictions such as cross-linking, geometrical confinement and interfaces.

2. Polymer melt dynamics and relaxometry

Field-cycling (FC) NMR relaxometry has become an important source of information on molecular dynamics in condensed matter, in particular, in liquids and polymer melts [1–3**]. As will be demonstrated, the method allows to cover all relaxation regimes relevant to polymer dynamics, such as segmental or "local" dynamics, Rouse as well as entanglement dynamics. Regarding the polymer specific dynamics also multi-quantum (MQ) NMR [4,5*,6] provides similar information and both FC and MQ NMR have recently been compared in detail [7*,8**]. Further NMR methods including field-gradient (FG) NMR may also contribute [9–12]. In contrast to rheology [13], for instance, NMR probes the dynamics on a molecular level and the term "molecular rheology" has been coined.

Field-cycling can be achieved by electronic or mechanical "switching" of the polarization, relaxation and detection B field. The magnetic field B fixes the Larmor frequency via $\omega = \gamma B$ (γ denotes the gyromagnetic ratio) and FC NMR relaxometry allows to measure the frequency dependence (dispersion) of the spin–lattice relaxation time T_1 (or T_2) by

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